

organic molecules have dozens of different bond stretching and bending motions, and thus have dozens of absorptions. On the one hand, this complexity is a problem because it generally limits the laboratory use of IR spectroscopy to pure samples of fairly small molecules—little can be learned from IR spectroscopy about large, complex biomolecules. On the other hand, this complexity is useful because an IR spectrum acts as a unique fingerprint of a compound. In fact, the complex region of the IR spectrum, from 1500 cm^{-1} to around 400 cm^{-1} , is called the *fingerprint region*. If two samples have identical IR spectra, they are almost certainly identical compounds.

Fortunately, we don't need to interpret an IR spectrum fully to get useful structural information. Most functional groups have characteristic IR absorption bands that don't change much from one compound to another. The C=O absorption of a ketone is almost always in the range 1680 to 1750 cm^{-1} ; the O–H absorption of an alcohol is almost always in the range 3400 to 3650 cm^{-1} ; the C=C absorption of an alkene is almost always in the range 1640 to 1680 cm^{-1} ; and so forth. By learning where characteristic functional-group absorptions occur, it's possible to get structural information from IR spectra. **TABLE 12-1** lists the characteristic IR bands of some common functional groups.

TABLE 12-1 Characteristic IR Absorptions of Some Functional Groups

Functional Group	Absorption (cm^{-1})	Intensity	Functional Group	Absorption (cm^{-1})	Intensity
Alkane			Amine		
C–H	2850–2960	Medium	N–H	3300–3500	Medium
Alkene			C–N	1030–1230	Medium
=C–H	3020–3100	Medium	Carbonyl compound		
C=C	1640–1680	Medium	C=O	1670–1780	Strong
Alkyne			Aldehyde	1730	Strong
≡C–H	3300	Strong	Ketone	1715	Strong
C≡C	2100–2260	Medium	Ester	1735	Strong
Alkyl halide			Amide	1690	Strong
C–Cl	600–800	Strong	Carboxylic acid	1710	Strong
C–Br	500–600	Strong	Carboxylic acid		
Alcohol			O–H	2500–3100	Strong, broad
O–H	3400–3650	Strong, broad	Nitrile		
C–O	1050–1150	Strong	C≡N	2210–2260	Medium
Arene			Nitro		
C–H	3030	Weak	NO ₂	1540	Strong
Aromatic ring	1660–2000	Weak			
	1450–1600	Medium			

Look at the IR spectra of hexane, 1-hexene, and 1-hexyne in **FIGURE 12-20** to see an example of how IR spectroscopy can be used. Although all three IR



tion at 2100 cm^{-1} and a terminal alkyne $\equiv\text{C}-\text{H}$ absorption at 3300 cm^{-1} .

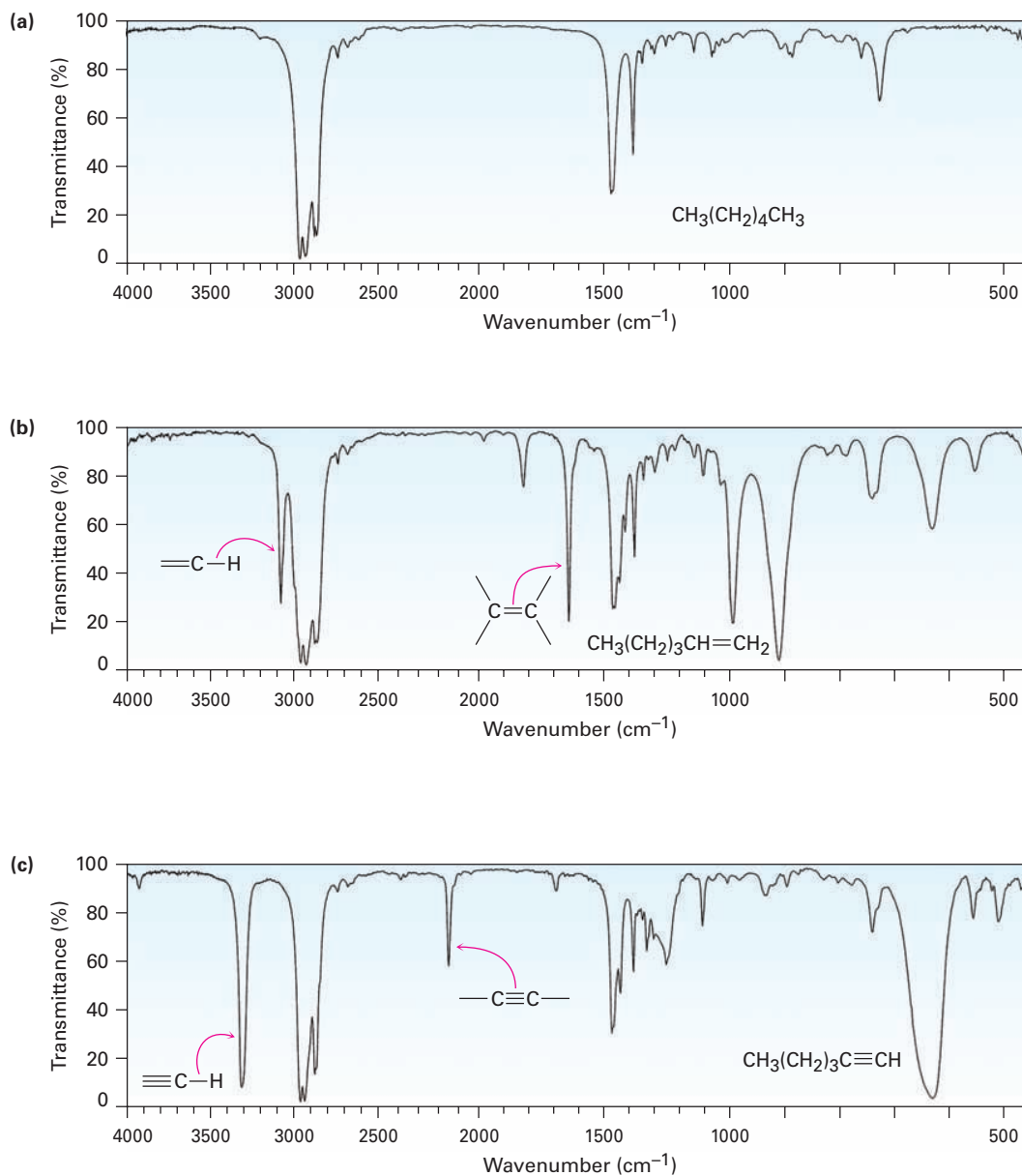


FIGURE 12-20 IR spectra of (a) hexane, (b) 1-hexene, and (c) 1-hexyne. Spectra like these are easily obtained from submilligram amounts of material in a few minutes using commercially available instruments.

N–H, C–H, and O–H single-bond stretching motions. N–H and O–H bonds absorb in the 3300 to 3600 cm^{-1} range; C–H bond stretching occurs near 3000 cm^{-1} .

- The region from 2500 to 2000 cm^{-1} is where triple-bond stretching occurs. Both $\text{C}\equiv\text{N}$ and $\text{C}\equiv\text{C}$ bonds absorb here.
- The region from 2000 to 1500 cm^{-1} is where double bonds ($\text{C}=\text{O}$, $\text{C}=\text{N}$, and $\text{C}=\text{C}$) absorb. Carbonyl groups generally absorb in the range 1680 to 1750 cm^{-1} , and alkene stretching normally occurs in the narrow range of 1640 to 1680 cm^{-1} .
- The region below 1500 cm^{-1} is the fingerprint portion of the IR spectrum. A large number of absorptions due to a variety of C–C, C–O, C–N, and C–X single-bond vibrations occur here.

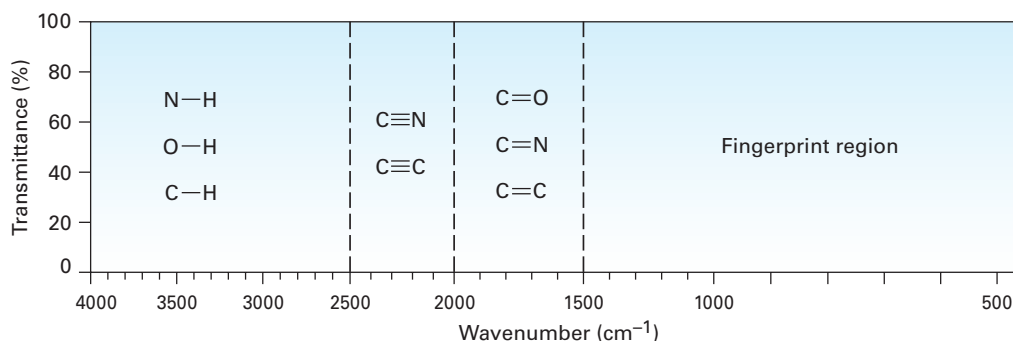


FIGURE 12-21 The four regions of the infrared spectrum: single bonds to hydrogen, triple bonds, double bonds, and fingerprint.

Why do different functional groups absorb where they do? As noted previously, a good analogy is that of two weights (atoms) connected by a spring (a bond). This type of system is a harmonic oscillator. In a harmonic oscillator, when a bond vibrates, its energy of vibration is continually and periodically changing from kinetic to potential energy and back again. The total amount of energy is proportional to the frequency of the vibration,

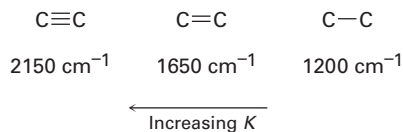
$$E_{\text{osc}} \propto h\nu_{\text{osc}}$$

The vibrational frequency of a harmonic oscillator is inversely proportional to the reduced mass of the oscillator, μ , and is directly proportional to the stiffness (strength) of the spring, K . The natural frequency of vibration of a bond is given by the equation

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

Springs connecting small weights vibrate faster than springs connecting large weights. Short, strong bonds vibrate at a higher energy and higher frequency

between heavier C, O, and N atoms.



Worked Example 12-4

Distinguishing Isomeric Compounds by IR Spectroscopy

Acetone (CH_3COCH_3) and 2-propen-1-ol ($\text{H}_2\text{C}=\text{CHCH}_2\text{OH}$) are isomers. How could you distinguish them by IR spectroscopy?

Strategy

Identify the functional groups in each molecule, and refer to Table 12-1.

Solution

Acetone has a strong $\text{C}=\text{O}$ absorption at 1715 cm^{-1} , while 2-propen-1-ol has an $-\text{OH}$ absorption at 3500 cm^{-1} and a $\text{C}=\text{C}$ absorption at 1660 cm^{-1} .

PROBLEM 12-7

What functional groups might the following molecules contain?

- (a) A compound with a strong absorption at 1710 cm^{-1}
- (b) A compound with a strong absorption at 1540 cm^{-1}
- (c) A compound with strong absorptions at 1720 cm^{-1} and 2500 to 3100 cm^{-1}

PROBLEM 12-8

How might you use IR spectroscopy to distinguish between the following pairs of isomers?

- (a) $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3OCH_3
- (b) Cyclohexane and 1-hexene
- (c) $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ and $\text{HOCH}_2\text{CH}_2\text{CHO}$

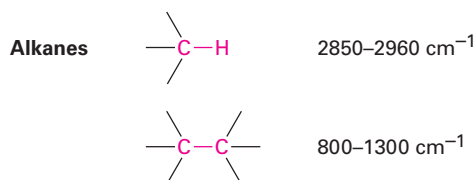
12-8 Infrared Spectra of Some Common Functional Groups

As each functional group is discussed in future chapters, the spectroscopic properties of that group will be described. For the present, we'll point out some distinguishing features of the hydrocarbon functional groups already studied and briefly preview some other common functional groups. We should

alkyne; if the spectrum has no absorption near 3400 cm^{-1} , the compound is not an alcohol; and so on.

Alkanes

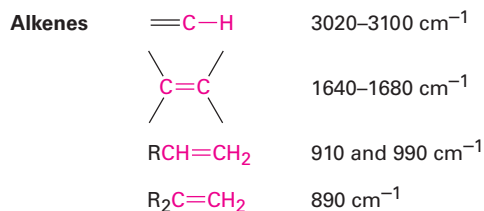
The IR spectrum of an alkane is fairly uninformative because no functional groups are present and all absorptions are due to C–H and C–C bonds. Alkane C–H bonds show a strong absorption from 2850 to 2960 cm^{-1} , and saturated C–C bonds show a number of bands in the 800 to 1300 cm^{-1} range. Since most organic compounds contain saturated alkane-like portions, most organic compounds have these characteristic IR absorptions. The C–H and C–C bands are clearly visible in the three spectra shown in Figure 12-20.



Alkenes

Alkenes show several characteristic stretching absorptions. Vinylic =C-H bonds absorb from 3020 to 3100 cm^{-1} , and alkene C=C bonds usually absorb near 1650 cm^{-1} , although in some cases their peaks can be rather small and difficult to see clearly when the alkene is symmetric, or nearly so. Both absorptions are visible in the 1-hexene spectrum in Figure 12-20b.

Alkenes have characteristic =C-H out-of-plane bending absorptions in the 700 to 1000 cm^{-1} range, thereby allowing the substitution pattern on a double bond to be determined (FIGURE 12-22). For example, monosubstituted alkenes such as 1-hexene show strong characteristic bands at 910 and 990 cm^{-1} , and 1,1-disubstituted alkenes ($\text{R}_2\text{C=CH}_2$) have an intense band at 890 cm^{-1} .





1660–2000 cm^{-1} (weak)
1450–1600 cm^{-1} (medium)

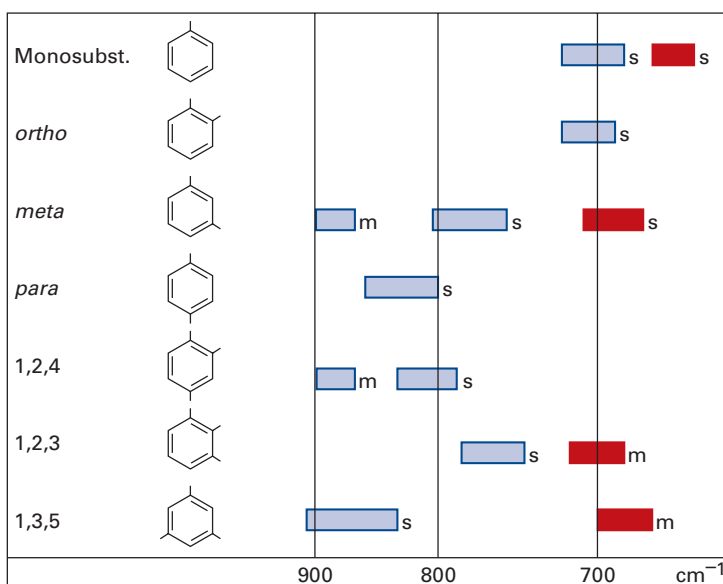


FIGURE 12-23 C–H out-of-plane bending vibrations for substituted benzenes.

The IR spectrum of phenylacetylene, shown in Figure 12-28 at the end of this section, gives an example, clearly showing the following absorbances: $\equiv\text{C}-\text{H}$ stretch at 3300 cm^{-1} , C–H stretches from the benzene ring at 3000 to 3100 cm^{-1} , C=C stretches of the benzene ring between 1450 and 1600 cm^{-1} , and out-of-plane bending of the ring's C–H groups, indicating monosubstitution at 750 cm^{-1} .

Alcohols

The O–H functional group of alcohols is easy to spot. Alcohols have a characteristic band in the range 3400 to 3650 cm^{-1} that is usually broad and intense. Hydrogen bonding between O–H groups is responsible for making the absorbance so broad. If an O–H stretch is present, it's hard to miss this band or to confuse it with anything else.

Alcohols —O—H $3400\text{--}3650\text{ cm}^{-1}$ (broad, intense)

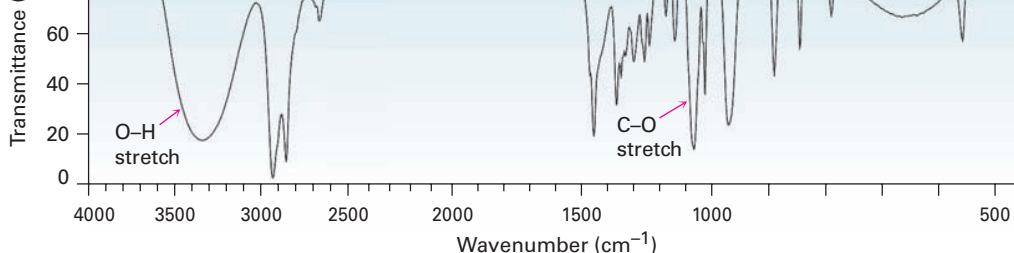
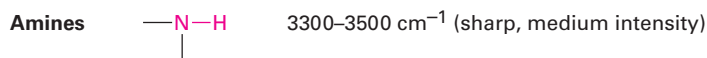


FIGURE 12-24 IR spectrum of cyclohexanol.

Amines

The N–H functional group of amines is also easy to spot in the IR, with a characteristic absorption in the 3300 to 3500 cm^{-1} range. Although alcohols absorb in the same range, an N–H absorption band is much sharper and less intense than an O–H band.



Primary amines exhibit two absorbances—one for the symmetric stretching mode and one for the asymmetric mode (**FIGURE 12-25**). Secondary amines only have one N–H stretching absorbance in this region.

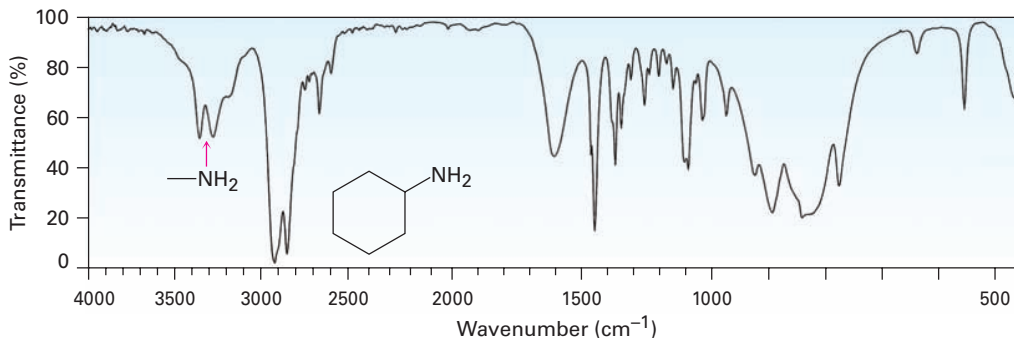
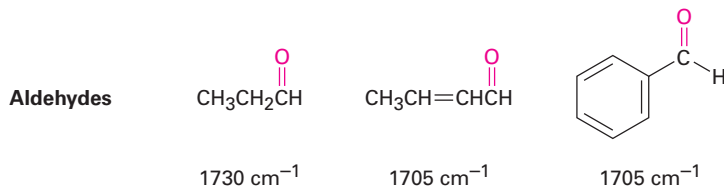


FIGURE 12-25 IR spectrum of cyclohexylamine.

Carbonyl Compounds

Carbonyl functional groups are the easiest to identify of all IR absorptions because of their sharp, intense peak in the range 1670 to 1780 cm^{-1} . Most important, the exact position of absorption within this range can often be used to identify the exact kind of carbonyl functional group—aldehyde, ketone, ester, and so forth. The principles of resonance, inductive electronic effects, and hydrogen bonding help us explain and understand the different frequencies at which different carbonyl groups absorb IR radiation.

and results in a lower vibrational frequency of the group.



The C–H group attached to the carbonyl is responsible for the characteristic IR absorbance for aldehydes at 2750 and 2850 cm^{-1} (FIGURE 12-26). Although these are not very intense, the absorbance at 2750 cm^{-1} in particular is helpful when trying to distinguish between an aldehyde and a ketone.

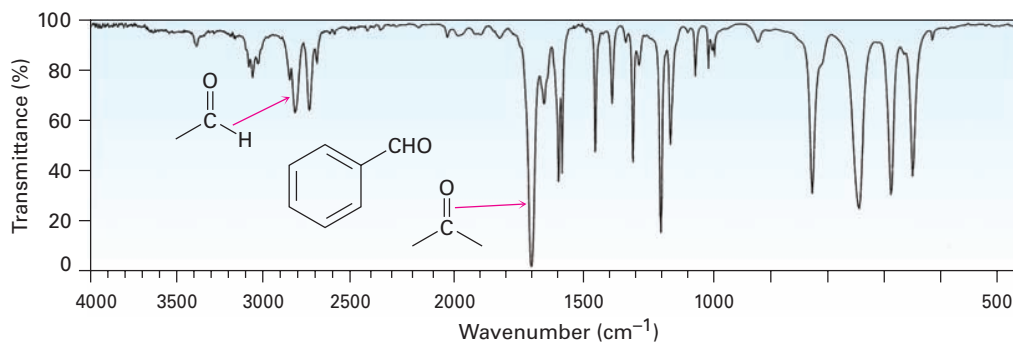
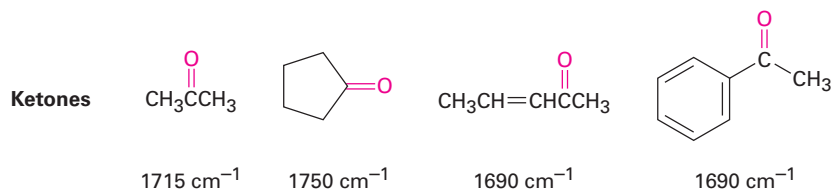


FIGURE 12-26 The IR spectrum of benzaldehyde.

KETONES Saturated open-chain ketones and six-membered cyclic ketones absorb at 1715 cm^{-1} . Ring strain stiffens the C=O bond, making five-membered cyclic ketones absorb at 1750 cm^{-1} and four-membered cyclic ketones absorb at 1780 cm^{-1} . Ketones next to a double bond or an aromatic ring absorb at 1690 cm^{-1} . As with an aldehyde, resonance delocalization of pi-electron density weakens the C=O a bit, causing it to absorb at a lower frequency. As a general rule, a conjugated carbonyl group absorbs IR radiation 20 to 30 cm^{-1} lower than the corresponding saturated carbonyl compound.

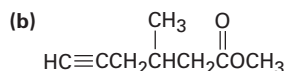
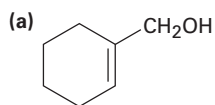


ESTERS Saturated esters absorb at 1735 cm^{-1} . In addition to the C=O absorbance, esters also have two strong absorbances in the 1300 to 1000 cm^{-1} range from the C–O portion of the functional group. Like the other carbonyl functional groups, esters next to either an aromatic ring or a double bond absorb at 1715 cm^{-1} , 20 to 30 cm^{-1} lower than a saturated ester.

Worked Example 12-5

Predicting IR Absorptions of Compounds

Where might the following compounds have IR absorptions?



Strategy

Identify the functional groups in each molecule, and then check Table 12-1 to see where those groups absorb.

Solution

- (a) *Absorptions:* 3400 to 3650 cm⁻¹ (O–H), 3020 to 3100 cm⁻¹ (=C–H), 1640 to 1680 cm⁻¹ (C=C). This molecule has an alcohol O–H group and an alkene double bond.
- (b) *Absorptions:* 3300 cm⁻¹ (≡C–H), 2100 to 2260 cm⁻¹ (C≡C), 1735 cm⁻¹ (C=O). This molecule has a terminal alkyne triple bond and a saturated ester carbonyl group.

Worked Example 12-6

Identifying Functional Groups from an IR Spectrum

The IR spectrum of an unknown compound is shown in **FIGURE 12-27**. What functional groups does the compound contain?

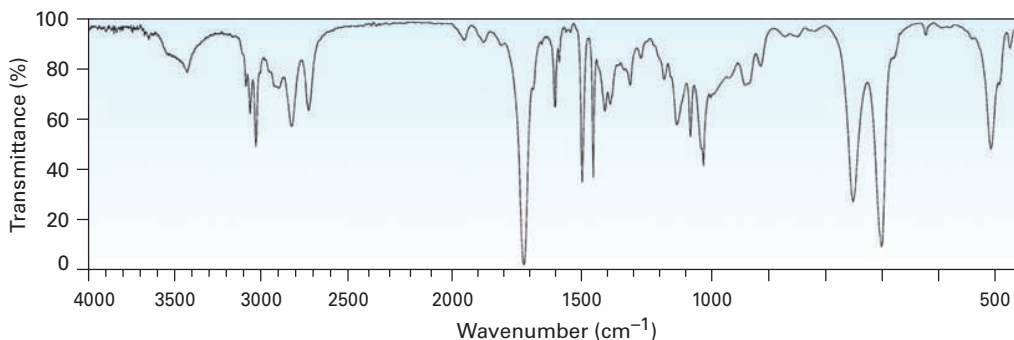
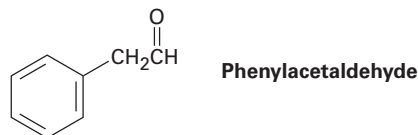


FIGURE 12-27 IR spectrum for Worked Example 12-6.

Strategy

All IR spectra have many absorptions, but those useful for identifying specific functional groups are usually found in the region from 1500 cm⁻¹ to 3300 cm⁻¹. Pay particular attention to the carbonyl region (1670 to

The spectrum shows an intense absorption at 1725 cm^{-1} due to a carbonyl group (perhaps an aldehyde, $-\text{CHO}$), a series of weak absorptions from 1800 to 2000 cm^{-1} characteristic of aromatic compounds, and a $\text{C}-\text{H}$ absorption near 3030 cm^{-1} , also characteristic of aromatic compounds. In fact, the compound is phenylacetaldehyde.



PROBLEM 12-9

The IR spectrum of phenylacetylene is shown in **FIGURE 12-28**. What absorption bands can you identify?

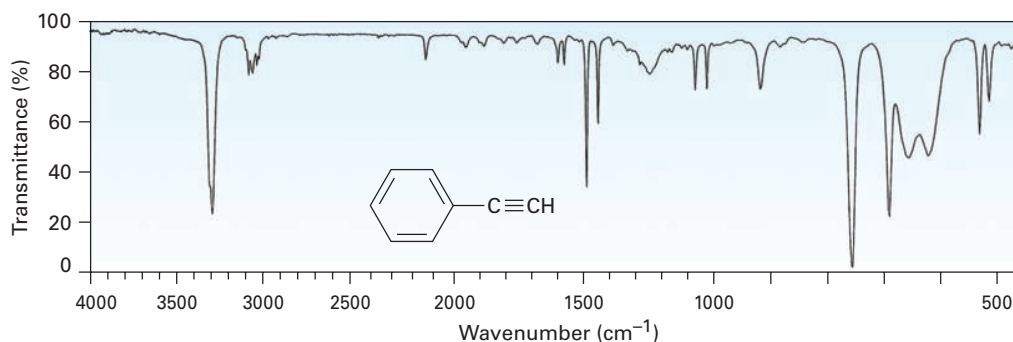
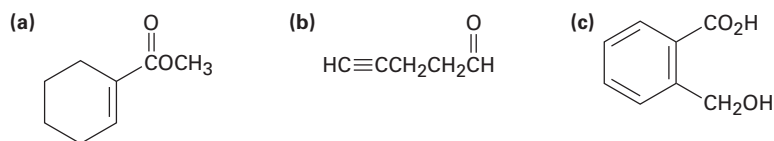


FIGURE 12-28 The IR spectrum of phenylacetylene, Problem 12-9.

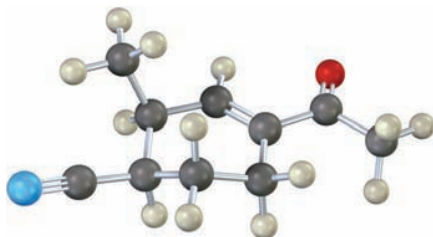
PROBLEM 12-10

Where might the following compounds have IR absorptions?



PROBLEM 12-11

Where might the following compound have IR absorptions?



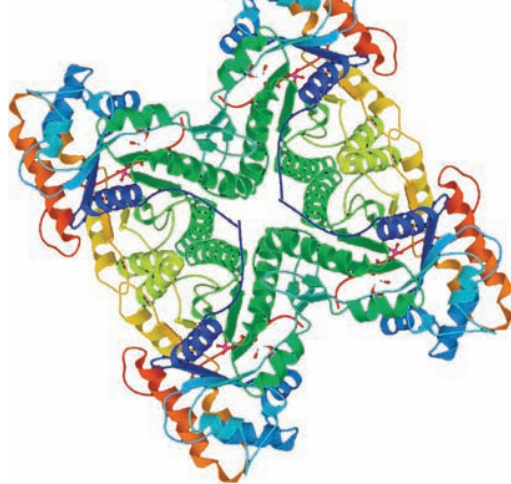
X-Ray Crystallography

The various spectroscopic techniques described in this and the next two chapters are enormously important in chemistry and have been fine-tuned to such a degree that the structure of almost any molecule can be found. Nevertheless, wouldn't it be nice if you could simply look at a molecule and "see" its structure with your eyes?

Determining the three-dimensional shape of an object around you is easy—you just look at it, let your eyes focus the light rays reflected from the object, and let your brain assemble the data into a recognizable image. If the object is small, you use a microscope and let the microscope lens focus the visible light. Unfortunately, there is a limit to what you can see, even with the best optical microscope. Called the diffraction limit, you can't see anything smaller than the wavelength of light you are using for the observation. Visible light has wavelengths of several hundred nanometers, but atoms in molecules have dimensions on the order of 0.1 nm. Thus, to "see" a molecule—whether a small one in the laboratory or a large, complex enzyme with a molecular weight in the tens of thousands—you need wavelengths in the 0.1 nm range, which corresponds to X rays.

Let's say that we want to determine the structure and shape of an enzyme or other biological molecule. The technique used is called *X-ray crystallography*. First, the molecule is crystallized (which often turns out to be the most difficult and time-consuming part of the entire process) and a small crystal of 0.4 to 0.5 mm on its longest axis is glued to the end of a glass fiber. The fiber and attached crystal are then mounted in an instrument called an X-ray diffractometer, which consists of a radiation source, a sample positioning and orienting device that can rotate the crystal in any direction, a detector, and a controlling computer.

Once mounted in the diffractometer, the crystal is irradiated with X rays, usually



PDB ID: 1ALD, Gamblin, S.J. Davies, G.J. Grimes, J.M. Jackson, R.M. Littlechild, J.A. (1991) *J. Mol. Biol.* 219: 573-576.

The structure of human muscle fructose-1,6-bisphosphate aldolase, as determined by X-ray crystallography and downloaded from the Protein Data Bank, 1ALD.

so-called $\text{CuK}\alpha$ radiation with a wavelength of 0.154 nm. When the X rays strike the enzyme crystal, they interact with electrons in the molecule and are scattered into a diffraction pattern which, when detected and visualized, appears as a series of intense spots against a null background.

Manipulation of the diffraction pattern to extract three-dimensional molecular data is a complex process, but the final result is an electron-density map of the molecule. Because electrons are largely localized around atoms, any two centers of electron density located within bonding distance of each other are assumed to represent bonded atoms, leading to a recognizable chemical structure. So important is this structural information for biochemistry that an online database of more than 100,000 biological substances has been created. Operated by Rutgers University and funded by the U.S. National Science Foundation, the Protein Data Bank (PDB) is a worldwide repository for processing and distributing three-dimensional structural data for biological macromolecules. We'll see how to access the PDB in the Chapter 26 *Something Extra*.

progression of chemistry and biochemistry. The structure of an organic molecule is usually determined using spectroscopic methods, including mass spectrometry and infrared spectroscopy. **Mass spectrometry (MS)** tells the molecular weight and formula of a molecule; **infrared (IR) spectroscopy** identifies the functional groups present in the molecule.

In small-molecule mass spectrometry, molecules are first ionized by collision with a high-energy electron beam. The ions then fragment into smaller pieces, which are magnetically sorted according to their mass-to-charge ratio (m/z). The ionized sample molecule is called the *molecular ion*, M^+ , and measurement of its mass gives the molecular weight of the sample. Structural clues about unknown samples can be obtained by interpreting the fragmentation pattern of the molecular ion. Mass-spectral fragmentations are usually complex, however, and interpretation is often difficult. In biological mass spectrometry, molecules are protonated using either electrospray ionization (ESI) or matrix-assisted laser desorption ionization (MALDI), and the protonated molecules are separated by time-of-flight (TOF) mass analysis.

Infrared spectroscopy involves the interaction of a molecule with **electromagnetic radiation**. When an organic molecule is irradiated with infrared energy, certain **frequencies** are absorbed by the molecule. The frequencies absorbed correspond to the amounts of energy needed to increase the amplitude of specific molecular vibrations such as bond stretching and bending. Since every functional group has a characteristic combination of bonds, every functional group has a characteristic set of infrared absorptions. For example, the terminal alkyne $\equiv\text{C}-\text{H}$ bond absorbs IR radiation of 3300 cm^{-1} , and the alkene $\text{C}=\text{C}$ bond absorbs in the range 1640 to 1680 cm^{-1} . By observing which frequencies of infrared radiation are absorbed by a molecule and which are not, it's possible to determine the functional groups a molecule contains.

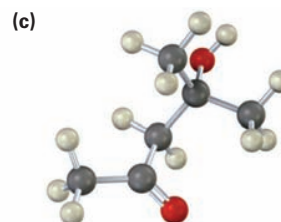
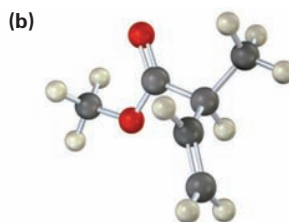
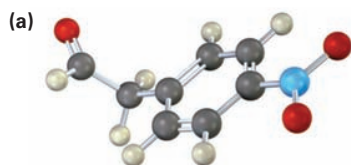
base peak ,	356
electromagnetic spectrum ,	
368	
frequency , ν ,	369
hertz , Hz,	369
infrared (IR) spectroscopy ,	
371	
mass spectrometry (MS) ,	355
parent peak ,	357
quadrupole mass analyzer ,	
356	
wavelength , λ ,	369
wavenumber $\tilde{\nu}$,	371

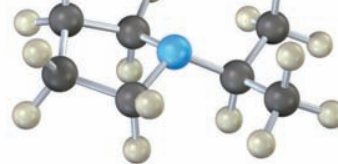
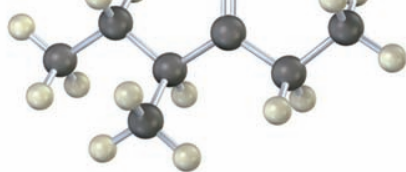
EXERCISES

VISUALIZING CHEMISTRY

(Problems 12-1–12-11 appear within the chapter.)

12-12 Where in the IR spectrum would you expect each of the following molecules to absorb?





ADDITIONAL PROBLEMS

Mass Spectrometry

- 12-14** Propose structures for compounds that fit the following mass-spectral data:
- (a) A hydrocarbon with $M^+ = 132$ (b) A hydrocarbon with $M^+ = 166$
(c) A hydrocarbon with $M^+ = 84$
- 12-15** Write molecular formulas for compounds that show the following molecular ions in their high-resolution mass spectra, assuming that C, H, N, and O might be present. The exact atomic masses are: 1.007 83 (^1H), 12.000 00 (^{12}C), 14.003 07 (^{14}N), 15.994 91 (^{16}O).
- (a) $M^+ = 98.0844$ (b) $M^+ = 123.0320$
- 12-16** Camphor, a saturated monoketone from the Asian camphor tree, is used among other things as a moth repellent and as a constituent of embalming fluid. If camphor has $M^+ = 152.1201$ by high-resolution mass spectrometry, what is its molecular formula? How many rings does camphor have?
- 12-17** The *nitrogen rule* of mass spectrometry says that a compound containing an odd number of nitrogens has an odd-numbered molecular ion. Conversely, a compound containing an even number of nitrogens has an even-numbered M^+ peak. Explain.
- 12-18** In light of the nitrogen rule mentioned in Problem 12-17, what is the molecular formula of pyridine, $M^+ = 79$?
- 12-19** Nicotine is a diamino compound isolated from dried tobacco leaves. Nicotine has two rings and $M^+ = 162.1157$ by high-resolution mass spectrometry. Give a molecular formula for nicotine, and calculate the number of double bonds.
- 12-20** The hormone cortisone contains C, H, and O, and shows a molecular ion at $M^+ = 360.1937$ by high-resolution mass spectrometry. What is the molecular formula of cortisone? (The degree of unsaturation for cortisone is 8.)

At what masses do the molecular ions occur for the following formulas? What are the relative percentages of each molecular ion?

(a) Bromomethane, CH_3Br (b) 1-Chlorohexane, $\text{C}_6\text{H}_{13}\text{Cl}$

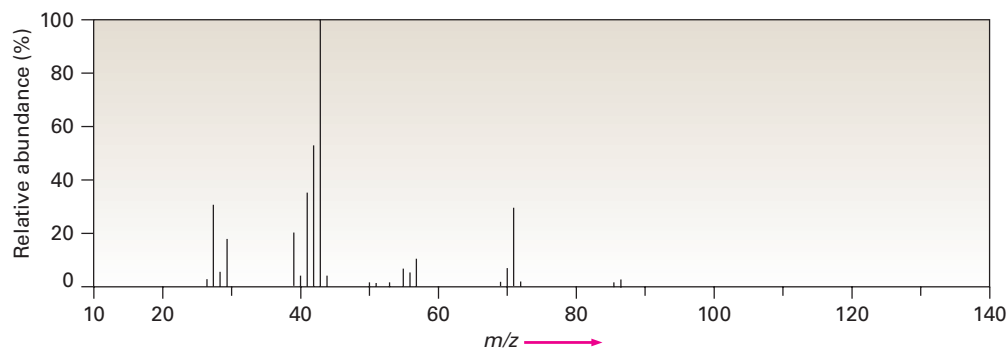
12-22 By knowing the natural abundances of minor isotopes, it's possible to calculate the relative heights of M^+ and $M + 1$ peaks. If ^{13}C has a natural abundance of 1.10%, what are the relative heights of the M^+ and $M + 1$ peaks in the mass spectrum of benzene, C_6H_6 ?

12-23 Propose structures for compounds that fit the following data:

(a) A ketone with $M^+ = 86$ and fragments at $m/z = 71$ and $m/z = 43$

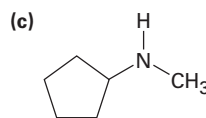
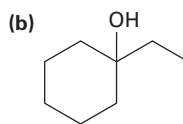
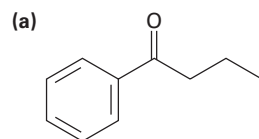
(b) An alcohol with $M^+ = 88$ and fragments at $m/z = 73$, $m/z = 70$, and $m/z = 59$

12-24 2-Methylpentane (C_6H_{14}) has the mass spectrum shown. Which peak represents M^+ ? Which is the base peak? Propose structures for fragment ions of $m/z = 71$, 57, 43, and 29. Why does the base peak have the mass it does?

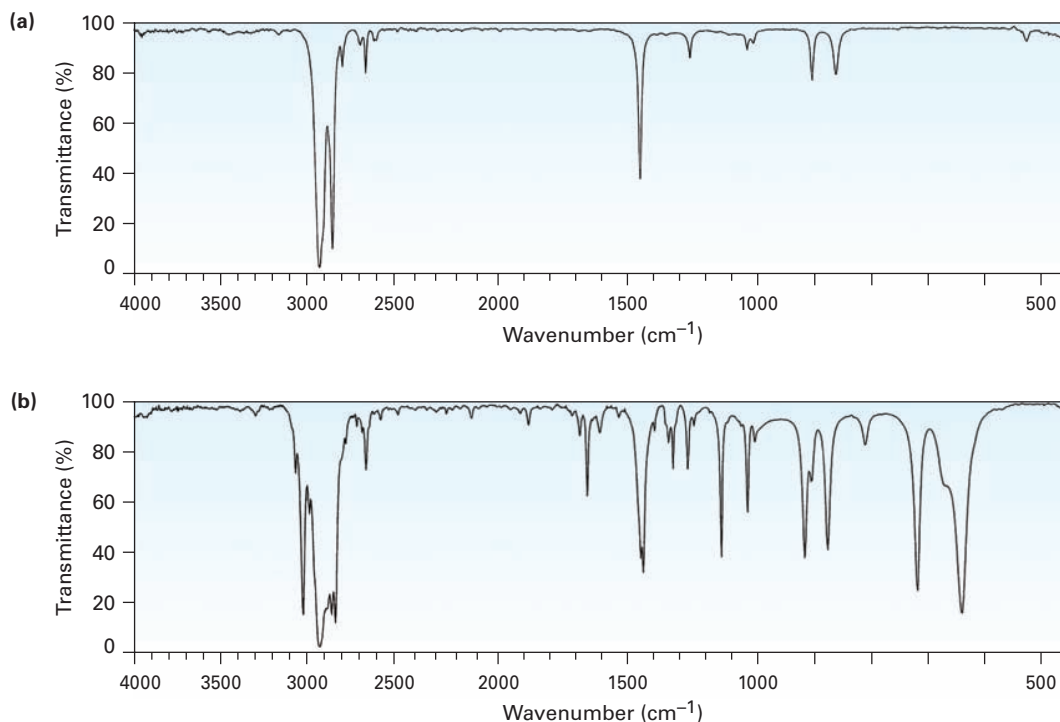


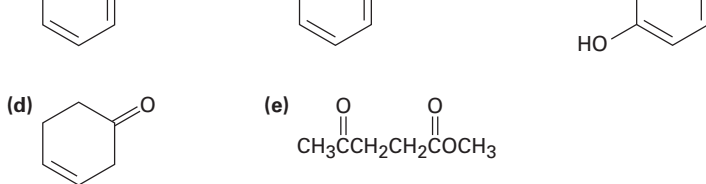
12-25 Assume that you are in a laboratory carrying out the catalytic hydrogenation of cyclohexene to cyclohexane. How could you use a mass spectrometer to determine when the reaction is finished?

12-26 What fragments might you expect in the mass spectra of the following compounds?

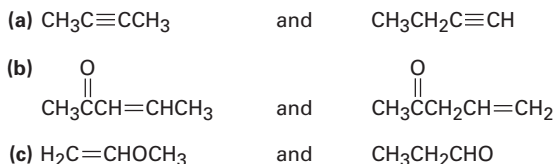


- 12-28** Would you expect two enantiomers such as (*R*)-2-bromobutane and (*S*)-2-bromobutane to have identical or different IR spectra? Explain.
- 12-29** Would you expect two diastereomers such as *meso*-2,3-dibromobutane and (2*R*,3*R*)-dibromobutane to have identical or different IR spectra? Explain.
- 12-30** Propose structures for compounds that meet the following descriptions:
- (a) C_5H_8 , with IR absorptions at 3300 and 2150 cm^{-1}
 - (b) C_4H_8O , with a strong IR absorption at 3400 cm^{-1}
 - (c) C_4H_8O , with a strong IR absorption at 1715 cm^{-1}
 - (d) C_8H_{10} , with IR absorptions at 1600 and 1500 cm^{-1}
- 12-31** How could you use infrared spectroscopy to distinguish between the following pairs of isomers?
- (a) $HC\equiv CCH_2NH_2$ and $CH_3CH_2C\equiv N$
 - (b) CH_3COCH_3 and CH_3CH_2CHO
- 12-32** Two infrared spectra are shown. One is the spectrum of cyclohexane, and the other is the spectrum of cyclohexene. Identify them, and explain your answer.

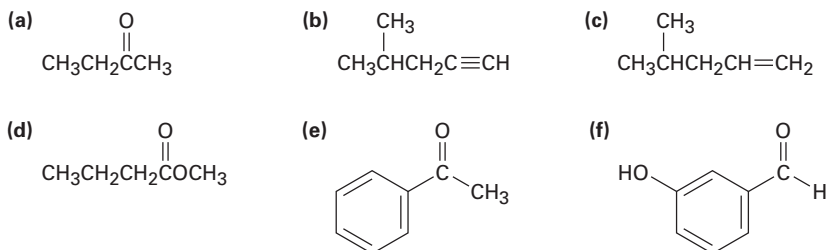




12-34 How would you use infrared spectroscopy to distinguish between the following pairs of constitutional isomers?



12-35 At what approximate positions might the following compounds show IR absorptions?



12-36 Assume that you are carrying out the dehydration of 1-methylcyclohexanol to yield 1-methylcyclohexene. How could you use infrared spectroscopy to determine when the reaction is complete?

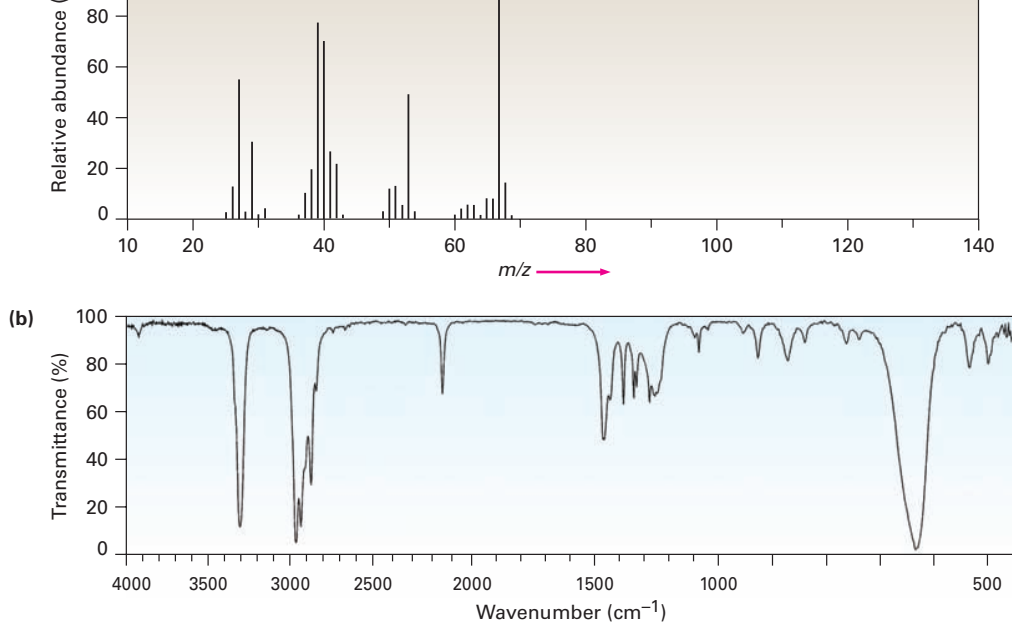
12-37 Assume that you are carrying out the base-induced dehydrobromination of 3-bromo-3-methylpentane (Section 11-7) to yield an alkene. How could you use IR spectroscopy to tell which of three possible elimination products is formed, if one includes *E/Z* isomers?

General Problems

12-38 Which is stronger, the C=O bond in an ester (1735 cm^{-1}) or the C=O bond in a saturated ketone (1715 cm^{-1})? Explain.

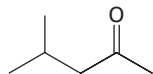
12-39 Carvone is an unsaturated ketone responsible for the odor of spearmint. If carvone has $M^+ = 150$ in its mass spectrum and contains three double bonds and one ring, what is its molecular formula?

12-40 Carvone (Problem 12-39) has an intense infrared absorption at 1690 cm^{-1} . What kind of ketone does carvone contain?

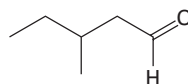


(b) A non-optically active compound C_5H_9N with an IR absorption at 2215 cm^{-1}

- 12-44** 4-Methyl-2-pentanone and 3-methylpentanal are isomers. Explain how you could tell them apart, both by mass spectrometry and by infrared spectroscopy.

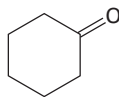


4-Methyl-2-pentanone

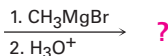


3-Methylpentanal

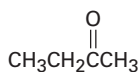
- 12-45** Grignard reagents undergo a general and very useful reaction with ketones. Methylmagnesium bromide, for example, reacts with cyclohexanone to yield a product with the formula $C_7H_{14}O$. What is the structure of this product if it has an IR absorption at 3400 cm^{-1} ?



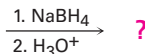
Cyclohexanone



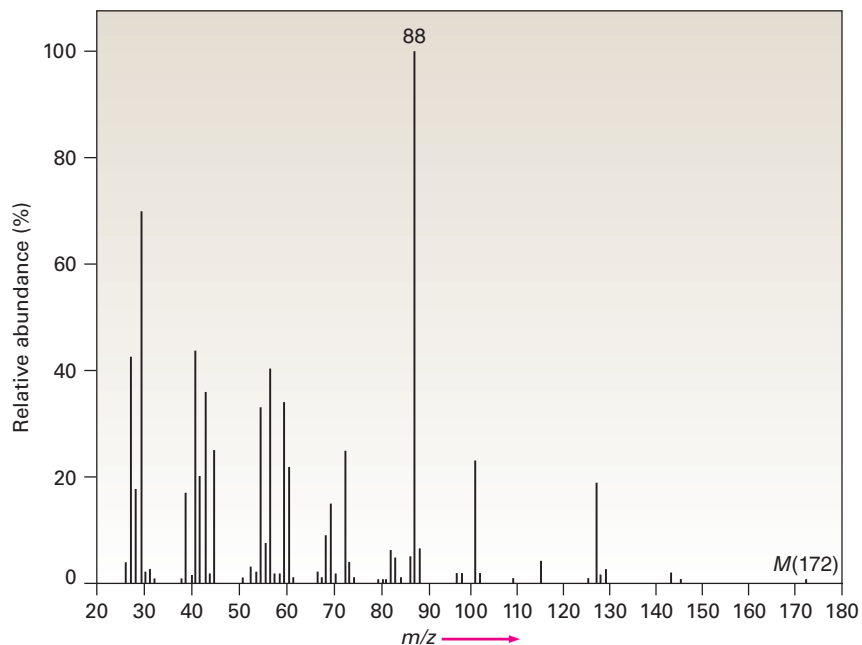
- 12-46** Ketones undergo a reduction when treated with sodium borohydride, $NaBH_4$. What is the structure of the compound produced by reaction of 2-butanone with $NaBH_4$ if it has an IR absorption at 3400 cm^{-1} and $M^+ = 74$ in the mass spectrum?



2-Butanone



- 12-47** Nitriles, $R-C\equiv N$, undergo a hydrolysis reaction when heated with aqueous acid. What is the structure of the compound produced by hydrolysis of propanenitrile, $CH_3CH_2C\equiv N$, if it has IR absorptions from $2500\text{--}3100\text{ cm}^{-1}$ and at 1710 cm^{-1} , and has $M^+ = 74$?



12-49 The infrared spectrum of the compound with the mass spectrum shown below has a medium-intensity peak at about 1650 cm^{-1} . There is also a C–H out-of-plane bending peak near 880 cm^{-1} . Propose a structure consistent with the data.

